Supporting Information for

Unusual Synergistic Effects Upon Incorporation of Fe and/or Ni Into Mesoporous Co₃O₄ for Enhanced Oxygen Evolution

Experimental

Reagents

All reagents were of analytical grade and used without further purification. Nickel (II) nitrate hexahydrate, iron (III) nitrate hexahydrate, potassium hydroxide and sodium hydroxide are purchased from Ajax Finechem Co., Ltd. Cobalt (II) nitrate hexahydrate and Nafion 117 (5 wt%) were purchased from Sigma-Aldrich. Water used throughout this study was purified by a Milli-Q water purification system, and had a resistance of 18 M Ω at 25 °C.

Electrocatalysts synthesis

Preparation of mesoporous silica template

Cubic well-ordered silica template (KIT-6) was prepared according to a previous study.¹ Concisely, preparation started with dissolving 1.0 g of Pluronic P123 (EO₂₀PO₇₀EO₂₀) in 35 mL 0.6 M hydrochloric acid. The mixture was then stirred at 35 °C for 30 min followed by the addition of 1.0 g of n-butanol. The mixture was continued stirring until forming homogenous solution. After that, 2.08 g of tetraethyl orthosilicate (TEOS) was added into the solution followed by another 24-hour stirring at 35 °C. The resultant mixture was transferred into a 48 mL Teflon-lined autoclave and heated at 100 °C in an oven for 24 hours. After the hydrothermal treatment, the powder was collected by filtration and washed several times with ethanol and water. Finally, the resulting powder was allowed to anneal at 550 °C for another 5 hours to remove the residual polymer template.

Preparation of mCo₃O₄, Fe/mCo₃O₄, Ni/mCo₃O₄ and FeNi/mCo₃O₄

The syntheses of mesoporous electrocatalysts were carried out via a nanocasting method using KIT-6 as the hard template. In a typical process, nitrates of the corresponding metal with a certain mass ratio were firstly dissolved in 5 mL absolutely ethanol followed by the

addition of 0.2 mg of KIT-6 template. The reaction mixture was then allowed to stir at 70 °C for several hours to completely evaporate the ethanol. The resultant solid was collected and calcinated at 300 °C for 3 hours to form metal oxides. The impregnation and crystallization processes were repeated once more to full fill the channels of KIT-6 with two-third of the metal precursor and silica template used in the first time. At last, the KIT-6 was removed by washing with 2 M hot NaOH solution followed by rinsing with Mill-Q water several times.

Electrochemical procedures

One mg of electrocatalyst and 10 μ L of Nafion solution were added into 200 μ L of water and isopropanol mixture (3:1, v/v), followed by thorough sonication until forming homogeneous ink. 3 μ L of the catalyst ink was then drop-casted onto the surface of glassy carbon (GC) electrodes, and left dry in air. The electrocatalytic performances of the catalysts obtained in this study were evaluated in a standard three-electrode electrochemical cell employing the catalyst loaded GC electrode as the working electrode, a Ag/AgCl (3 M KCl) as the reference electrode and a Pt wire as the counter electrode. All measurements were carried out in 1 M KOH solutions (pH = 14) at a scan rate of 5 mV s⁻¹. The potentials measured in this study were all referred to reversible hydrogen electrode (RHE) reference for comparison purposes according to equation 1.

$$E_{RHE} = E_{Ag/AgCl} + 0.197 + 0.059pH$$
(1)

For bulk water electrolysis, 100 μ L of the catalyst ink was drop-casted onto the surface of 0.5 cm² Teflon-line carbon fibre paper (CFP, Fuel Cell Store, USA), and the catalyst-loaded CFP was employed as the working electrode in an electrolysis cell as described somewhere else.² In the bulk water electrolysis, the potential was controlled at 1.67 V vs RHE, and the corresponding current density was recorded for a 33 hour-long session.

Rotating Pt ring/GC disc electrode (RRDE purchased from ALS Co., Ltd) was used to monitor the evolution of oxygen. Specifically, 5 μ L of the catalyst ink was drop-casted onto the GC disc of the RRDE. The potential of the Pt ring was set at 0.4 V to detect the oxygen generated on the disc electrode. The collection efficiency (*N*) of the RRDE is determined to be 28% according to the methods described previously.³ The faraday efficiency of the Fe/mCo₃O₄ catalyst was determined using stabilized current densities originated from oxygen evolution and oxygen reduction respectively. The Faraday efficiency of 99.1% can be obtained according to equation 2.

$$E = \frac{j_{ORR} \times N}{j_{OER}} \times 100\%$$
⁽²⁾

Where j_{ORR} is the stabilized current density of ORR, N is the collection efficiency, j_{OER} is the stabilized current density of OER.

The turnover frequency (TOF) of the catalyst is calculated according to equation 3:4

$$TOF = \frac{J \times A}{4 \times F \times m} \tag{3}$$

Where *J* is the current density at the overpotential of 400 mV in A cm⁻², A is the surface of the GC electrode in cm⁻², F is the Faraday constant with the value of 96485 C mol⁻¹ and m is the mole of the active Co determined by XPS.

Physical Characterizations

TEM images were carried out on a Philips CM 200 at 200 kV. Powder XRD were conducted on a PANalytical X'Pert instrument using Cu K α radiation (λ = 0.15418 nm) in the 2 θ range from 10° to 80° with a scanning step size of 0.01°.XPS was performed on Thermo ESCALA250i X-ray Photoelectron Spectrometer. N₂ adsorption-desorption results were obtained from a gas adsorption analyser NOV1200, demonstrating the porous structure of samples.



Figure S1. TEM images of (a) mCo_3O_4 , (b) Ni/ mCo_3O_4 , (c) - (d) FeNi/ mCo_3O_4 , (e) - (f) FemCo₃O₄



Figure S2. XRD of mCo₃O₄, Fe/mCo₃O₄, FeNi/mCo₃O₄ and Ni/mCo₃O₄.



Figure S3. (a) XPS survey (inset is the high resolution Fe 2p XPS), (b) Co 2p XPS of the Fe/mCo₃O₄ composite.



Figure S4. Co and Fe EDX mapping of Fe/Co₃O₄



Figure S5. Chronoamperometric curves obtained at the rotating Pt ring GC disc electrode for quantification of oxygen.



Fig. S6 Pre-oxidation peaks of mCo₃O₄ and Fe/mCo₃O₄



Figure S7. Tafel plot of Ni/mCo₃O₄ (blue curve) and FeNi/mCo₃O₄ (green curve)



Figure S8. Bulk water electrolysis using Fe/mCo_3O_4 at constant potential of 1.67 V vs. RHE in 1 M KOH solution. The electrolysis current fluctuates, owing to gas bubble formation, but doesn't degrade.

Sample	Onset	Over potential	$j (\mathrm{mA} \mathrm{cm}^2)$	Tafel	BET
	potential	(V)	(E = 1.67 V)	slope	SA
	(V)	$(j = 10 \text{ mA cm}^2)$		(mV/dec)	(m^{2}/g)
mCo ₃ O ₄	1.56	1.65	14.5	71.6	54
Fe/ mCo ₃ O ₄	1.52	1.61	30.0	60.0	135
Ni/ mCo ₃ O ₄	1.56	1.64	19.0	88	144
FeNi/	1.56	1.64	20.0	87.2	136
mCo ₃ O ₄					

Table S1. Over potential (at 0 and 10 mA cm²), current density (at 1.65 V vs. RHE), Tafel slop and surface area of as-prepared catalysts

1. F. Kleitz, S. H. Choi and R. Ryoo, *Chem Commun*, 2003, 2136-2137.

2. X. Y. Lu and C. Zhao, *J Mater Chem A*, 2013, **1**, 12053-12059.

 O. Solorza-Feria, S. Ramirez-Raya, R. Rivera-Noriega, E. Ordonez-Regil and S. M. Fernandez-Valverde, *Thin Solid Films*, 1997, **311**, 164-170.

M. Gong, Y. G. Li, H. L. Wang, Y. Y. Liang, J. Z. Wu, J. G. Zhou, J. Wang, T. Regier, F. Wei and H. J. Dai, *J Am Chem Soc*, 2013, 135, 8452-8455.